

PATENT ABSTRACTS OF JAPAN

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(54) PRODUCTION OF BROMINATED POLYSTYRENE

(57)Abstract:

PURPOSE: To obtain a brominated polystyrene which has a satisfactory hue and excellent heat resistance and is widely usable as a flame retardant.

CONSTITUTION: This production method comprises reacting a polystyrene with bromine in a halogenated hydrocarbon solvent using a catalyst comprising a combination of an aluminum halide and an aluminum powder.

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CLAIMS

[Claim(s)]

[Claim 1] The manufacture approach of the bromination polystyrene characterized by using aluminum halide and an aluminium powder as a catalyst in the approach of making polystyrene and a bromine reacting in a halogenated hydrocarbon solvent, and manufacturing bromination polystyrene.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the bromination approach of polystyrene. Furthermore, it is related with the approach of making polystyrene and a bromine reacting in a halogenated hydrocarbon solvent, and manufacturing bromination polystyrene in detail. The bromination polystyrene obtained by this invention is broadly used as a flame retarder for plastics.

[0002]

[Description of the Prior Art] Conventionally, as a manufacturing method of bromination polystyrene, the approach of carrying out the polymerization of the bromination styrene monomer is learned. The bromination polystyrene obtained by this approach can be said to be the approach excellent in the point that the bromination polystyrene of high bromine content can be manufactured by having the outstanding color tone and the outstanding thermal property, and using 3 bromination styrene for a monomer. However, this approach lacks in economical efficiency -- the process which removes the monomer which remains after that the bromination styrene monomer which is a raw material is expensive, and polymerization reaction termination is needed -- and practicality.

[0003] Furthermore, how to brominate polystyrene is also learned as the industrial manufacture approach of bromination polystyrene. This approach has the trouble which the bromination polystyrene of the color tone and the thermal property of it being not only economical, but having high bromine content and having excelled although it was the approach excellent in the point that bromine content can be adjusted to arbitration cannot acquire easily.

[0004] According to this approach, although two bromines per ring piece are permuted easily, if it is going to obtain the bromination polystyrene of further more high bromine content, not only bromination of the nucleus of polystyrene but bromination of a hydrocarbon principal chain and cutting will take place as side reaction, and the thermal resistance of the obtained bromination polystyrene will usually fall. When such bromination polystyrene is blended with thermoplastics, since the physical properties and appearance of the obtained mold goods falling and the bromination polystyrene obtained by doing in this way generate a hydrogen bromide on the occasion of a pyrolysis, it has the fault that the use field is extremely restricted on the occasion of practical use, such as corroding metal mold, at the time of fabrication.

[0005] Although there are an approach using the catalyst of low activity like 3 halogenation iron as an approach of solving these problems, a method of reducing the amount of catalysts, the approach of lowering reaction temperature, etc., by such approach, the problem of being unable to attain the desired bromine content to which reaction time becomes long occurs.

[0006] Furthermore, the bromination technique for solving these problems is indicated by many patent specifications. For example, in JP,1-57684,B, the method of using a bromine chloride for a brominating agent and using halogenation antimony for a catalyst is proposed. However, by this approach, there is a fault that a part of the production process of a bromine chloride being needed and bromination polystyrene obtained are chlorinated. Moreover, in JP,61-34723,B, under existence of the nucleophilicity agent like water, although the approach of brominating adjusting catalytic activity is proposed, adjustment of a minute amount moisture content is needed, and a problem is in practicality. Moreover, although the method of using the double salt of an alkali-metal halogenide and halogenation iron as a catalyst is proposed in JP,62-58604,B, the bromination polystyrene of high bromine content cannot be obtained by this approach.

[0007]

[Problem(s) to be Solved by the Invention] This invention is faced brominating polystyrene and manufacturing bromination polystyrene, and does not have the above-mentioned fault, it is good and a hue aims at offering the

approach of manufacturing economically high bromine content polystyrene excellent in thermal resistance efficiently. [0008] Without extending reaction time by using aluminum halide and an aluminium powder for a catalyst, as a result of inquiring further paying attention to the ability to reduce the substantial amount of catalysts by using together aluminum halide and an aluminium powder for a catalyst as a result of attaining the above-mentioned purpose and inquiring wholeheartedly, this invention persons of a hue are good, and reach the approach of bromination polystyrene **** this invention that thermal resistance has also been improved remarkably.

[0009]

[Means for Solving the Problem] This invention relates to the bromination approach of the polystyrene characterized by using together aluminum halide and an aluminium powder as a catalyst in the approach of making polystyrene and a bromine reacting in a halogenated hydrocarbon solvent, and manufacturing bromination polystyrene.

[0010] Although there will be especially no limitation if it does not react with a bromine and deactivation of the catalyst is not carried out as a solvent used by this invention, saturation aliphatic series halogenated hydrocarbon, such as a methylene chloride, a dichloroethane, trichloroethane, dichloro dibromoethane, dibromoethane, tetrabromo ethane, and a carbon tetrachloride, is mentioned, for example. These may be the solvents which carried out dehydration processing not only of an anhydrous solvent but the recovery solvent, and were substantially changed into the anhydrous condition. Also in these, a methylene chloride is desirable practically.

[0011] As polystyrene used by this invention, about 10,000 to 500,000 thing is used with weight average molecular weight, and the thing of 20,000-250,000 is desirable especially.

[0012] Although it is desirable to use 1-3 mols to one mol of benzene rings of polystyrene as for the bromine used as a brominating agent by this invention, in order to manufacture the high bromination polystyrene of especially bromine content, it is desirable to use a 2-3-mol bromine.

[0013] The description of this invention is to use together aluminum halide and an aluminium powder as a catalyst. As aluminum halide, although an aluminum chloride, the aluminium bromide, and an aluminium iodide are mentioned, especially an aluminum chloride is desirable. Although there is especially no limitation as a gestalt of aluminum halide and the aluminium powder used together, in consideration of distribution in side reaction and reaction mixture etc., the thing of the shape of a high grade and impalpable powder is desirable. Moreover, you may add with aluminum halide before bromine dropping, and in the middle of bromine dropping, although any are sufficient as the addition stage of an aluminium powder after bromine dropping termination, it is desirable [a stage] to add to aluminum halide and coincidence before bromine dropping practically. since reaction time will become long if it is not much alike and there is little amount of the catalyst used -- practically -- the sum of the stoichiometry of aluminum halide and an aluminium powder -- per one mol of rings of polystyrene -- usually -- 0. 1-10-mol % -- it is 1-5-mol % preferably. Moreover, although the rates of aluminum halide and an aluminium powder are 1/0.01-0.01/1 in a weight ratio, since there is an inclination for coloring of the bromination polystyrene which will be obtained if the rate of aluminum is made high to become large, they are 1 / 0.1 - 1/1 preferably.

[0014] A bromine is dropped, after usually dissolving polystyrene in the above-mentioned organic solvent and throwing in the aluminum halide and the aluminium powder of the specified quantity subsequently, if it is in this invention. A bromination reaction is performed by dropping a bromine, holding preferably 0-30 degrees C of temperature at 5-20 degrees C. There is an inclination for coloring of the bromination polystyrene from which it will be obtained if a rate of reaction becomes slow at less than 0 degree C and reaction temperature is higher than 30 degrees C to become large. It holds at further 5-15 degrees C after dropping termination, stirring is continued for 10 minutes - 2 hours, and a reaction is completed. After reaction termination, a reaction solution is thrown in underwater, or water is fed into a reaction solution, deactivation of the catalyst is carried out, a water layer is separated, an organic solvent layer is washed with water, and an impurity is removed. For isolating the bromination polystyrene contained in the organic solvent layer after washing, an organic solvent layer may be poured out into lower alcohol, such as the approach of arbitration, for example, a methanol etc., and the saturated aliphatic hydrocarbon of carbon numbers 5-8, and you may make it deposit, and a reaction solvent layer is poured out into warm water, and a solvent may be evaporated and may be deposited. Moreover, it is good also by the approach of distilling off a solvent under the vacuum like spray drying.

[0015] The bromination polystyrene obtained by the approach of this invention has 1-3 bromine atoms per ring of polystyrene, and since it excels in a hue or thermal resistance, they can be broadly used for it as flame retarders for plastics, such as a polycarbonate, polyester, polypropylene, styrene resin, and a polyamide.

[0016]

[Example] An example is raised to below and this invention is further explained to it. In addition, the following approach estimated the hue in an example, and thermal resistance.

[0017] Color Phase: The obtained bromination polystyrene was dissolved in the 50ml methylene chloride after 0.10g weighing capacity, and the hue (APHA) was measured for this solution as compared with the HAZEN standard color solution. It is shown that a hue is so good that a value is small.

[0018] Thermal resistance: With the 1090by TA instrument company B mold thermal-analysis system 951 mold TGA, the programming rate in nitrogen-gas-atmosphere mind of 20 degrees C / min estimated at loss-in-quantity temperature 3%.

[0019]

[Example 1] 530g of methylene chlorides and polystyrene [Dainippon Ink ERASUCHIREN 200 and weight-average-molecular-weight 55,000] 34g were taught to the 4 opening flask with a capacity of 1l. which attached the thermometer, the dropping funnel, and the cooling pipe, and after holding at 5-7 degrees C and throwing in 1.15g of bottom aluminum chlorides of stirring, and 0.07g of aluminium powders, it was dropped at 5-10 degrees C, having covered [139g] it for 45 minutes. It stirred after dropping termination for further 1 hour, and the reaction was completed. The obtained reaction solution was dropped at underwater [250ml] over 10 minutes, and deactivation of the catalyst was carried out. The water layer was removed, the organic solvent layer was further dropped [with 400ml water / after 2 times washing and filtration] over 1 hour under stirring into 400ml warm water (50-80 degrees C), the depositing solid-state was dried the ** exception, and bromination polystyrene (67% [of bromine content], 2.65Br objects) 94g of white was obtained. The hue of the obtained bromination polystyrene and the heat-resistant evaluation result were shown in Table 1.

[0020]

[Examples 2-4] It inquired by the same approach as an example 1 except having changed the amount of an aluminum chloride and the aluminium powder used. The hue of the bromination polystyrene obtained on that occasion and the heat-resistant evaluation result were combined, and were shown in Table 1.

[0021]

[The example 1 of a comparison] 530g of methylene chlorides and polystyrene [Dainippon Ink ERASUCHIREN 200 and weight-average-molecular-weight 55,000] 34g were taught to the 4 opening flask with a capacity of 1l. which attached the thermometer, the dropping funnel, and the cooling pipe, and after holding at 5-7 degrees C and supplying 1.70g of bottom aluminum chlorides of stirring, it was dropped at 5-10 degrees C, having covered [139g] it for 45 minutes. It stirred after dropping termination for further 1 hour, and the reaction was completed. The obtained reaction solution was dropped at underwater [250ml] over 10 minutes, and deactivation of the catalyst was carried out. The water layer was removed, the organic solvent layer was further dropped [with 400ml water / after 2 times washing and filtration] over 1 hour under stirring into 400ml warm water (50-80 degrees C), the depositing solid-state was dried the ** exception, and bromination polystyrene (67% [of bromine content], 2.65Br objects) 92g of white was obtained. The hue of the obtained bromination polystyrene and the heat-resistant evaluation result were written together with the example to Table 1.

[0022]

[The example 2 of a comparison] 530g of methylene chlorides and polystyrene [Dainippon Ink ERASUCHIREN 200 and weight-average-molecular-weight 55,000] 34g were taught to the 4 opening flask with a capacity of 1l. which attached the thermometer, the dropping funnel, and the cooling pipe, and after holding at 7 degrees C and supplying 1.49g of bottom aluminum chlorides of stirring, it was dropped at 5-10 degrees C, having covered [139g] it for 45 minutes. It stirred after dropping termination for further 1 hour, and the reaction was completed. The obtained reaction solution was dropped at underwater [250ml] over 10 minutes, and deactivation of the catalyst was carried out. At this time, the water layer was ****(ed) brown and survival of an unreacted bromine was checked. The water layer was removed, the organic solvent layer was further dropped [with 400ml water / after 2 times washing and filtration] over 1 hour under stirring into 400ml warm water (50-80 degrees C), the depositing solid-state was dried the ** exception, and bromination polystyrene (65% [of bromine content], 2.35Br objects) 88g of white was obtained. The hue of the obtained bromination polystyrene and the heat-resistant evaluation result were written together to Table 1.

[0023]

[Table 1]

	触媒量		色相	耐熱性	Br Cont.	収量
	AlCl ₃ [g]	Al [g]	(APHA) [-]	TGA-3%減量 [°C]	カリウス法 [%]	[g]
実施例 1	1.15	0.07	25	385	67	94
2	1.00	0.10	10	383	67	95
3	0.87	0.13	35	384	67	94
4	0.76	0.15	35	386	67	92
比較例 1	1.70	-	15	372	67	92
2	1.49	-	35	125	65	88

[0024]

[Effect of the Invention] A hue and thermal resistance are excellent in the bromination polystyrene obtained by the approach of this invention, and it can be broadly used as a flame retarder. Especially, the approach of this invention faces brominating polystyrene and demonstrates remarkable effectiveness to a heat-resistant improvement of the bromination polystyrene obtained.

[Translation done.]